

# Ruthenium Catalyzed Metathesis of Conjugated Polyenes

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Dedication ((optional))

**Abstract:** In the past decade numerous examples of olefin metathesis-based chemical technologies have been developed making olefin metathesis increasingly dominant in several sustainable and green chemical processes. In spite of the wide application profile, conjugated olefin metathesis - especially conjugated polyene metathesis - is an area of great interest with little exploration. Metathesis of conjugated polyenes is often cumbersome and requires high catalyst loading, most probably due to formation of less or inactive ruthenium  $\eta^3$ -vinylcarbene intermediates. Mechanistic understanding and development of a new highly active catalytic system for olefin metathesis will open new areas for exploration. For example, the utilization of petrochemical by products such as cyclopentadiene or a new way in utilizing butadiene, isoprene and conjugated electron systems containing natural products such as terpenes and polyunsaturated fatty acids. Understanding the mechanism of ruthenium  $\eta^1$  -  $\eta^3$  - vinylcarbene interconversion may open the way to the development of new generation ruthenium-based latent metathesis catalyst systems. This review summarizes the most relevant pioneer work focused on metathesis of conjugated polyenes in order to open new ideas for the development of forthcoming latent metathesis catalysts and to explore different application areas.

## 1. Introduction

Olefin metathesis is one of the fundamentally novel organic reactions that was discovered in the 1950's by industrial chemists. This new industrial avenue has led to the synthesis and development of innovative materials, petrochemicals and pharmaceutical drugs.<sup>1</sup> The first reported homogeneous metathesis catalysts were based on a multicomponent system, whereby the catalytically active species were formed *in situ* in the reaction mixture. Mostly high oxidation state transition metal halides ( $\text{MoCl}_5$ ,  $\text{WCl}_6$ ) and main group metal alkyl co-catalyst ( $\text{Al}(\text{C}_2\text{H}_5)_3$ ,  $\text{BuSn}_4$ ) were used.<sup>2</sup> Nevertheless, lengthy initiation reaction times and harsh reaction conditions of these complexes limited their application to mainly petrochemical conversions. The first single component complexes were based on Ti,<sup>3</sup> W<sup>4</sup> and Mo<sup>5</sup> systems. These catalyst systems showed high activity, however, they suffered from oxygen and moisture sensitivity and low functional group tolerance. To overcome these limitations ruthenium based complexes were introduced for olefin

metathesis. Ru based catalysts show high reactivity towards olefin bonds while remaining tolerant toward moisture, oxygen and several functional groups. To date, Ru appears to be one of the ideal metals for metathesis reactions.<sup>6</sup>

Olefin metathesis can be classified into five groups: (1) cross metathesis (CM); (2) ring-closing metathesis (RCM); (3) ring-opening cross-metathesis (ROCM); (4) ring-opening metathesis polymerization (ROMP) and (5) acyclic diene metathesis polymerization (ADMET). Some examples are selected for each group and will be discussed in section 2.

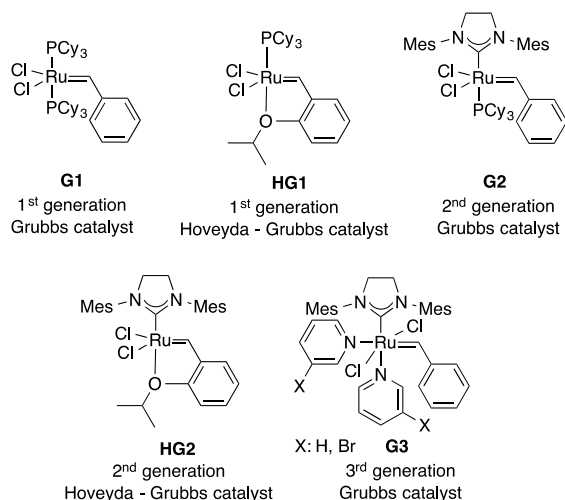
Cross metathesis reactions usually generate acyclic olefins with desired molecular size of linear internal olefins.<sup>7</sup> In RCM, two terminal-olefinic bond-containing molecules react in the presence of a catalyst resulting in macrocycles with the release of smaller olefins (e.g. ethylene). This type of reaction has a wide range of applications, especially in the synthesis of bioactive materials such as alkaloids and different pharmaceutical intermediates.<sup>8</sup> ROCM reactions are actually the opposite of ring-closing metathesis. Cycloolefins in the presence of metathesis catalysts and excess of ethylene or linear olefins give acyclic dienes. On the other hand, in ROMP strained cyclic olefins tend to open up and polymerize leading to the formation of polyolefins. This particular type of reaction has broad application in the synthesis of innovative materials, such as environmentally friendly synthetic rubbers or biopolymers.<sup>9</sup> Moreover, they can also be used in the pharmaceutical industry for synthesising biomaterials such as well-defined poly(vinyl alcohol) co-polymers.<sup>10</sup> ADMET polymerization is used to polymerize terminal dienes and polyenes. This polymerization is considered to be a step growth- condensation polymerization, which is driven by the release of ethylene gas.<sup>11</sup> It is also worth to mention that there is another subtype of olefin metathesis known as enyne metathesis. The reaction takes place between an alkene and alkyne and the driving force for the reaction is the formation of a thermodynamically favoured conjugated dienes.<sup>12</sup>

A wide range of catalysts has been shown to initiate metathesis reactions in the past. However, industrial applications of olefin metathesis reactions only evolved when a stable, highly efficient and well-defined systems appeared. The most active and widely used catalysts are molybdenum- or ruthenium-based systems. The molybdenum-based systems are sometimes more active than the ruthenium counterpart; however, they suffer from high oxygen and moisture sensitivity. Therefore, their industrial and large-scale applications are often limited. The ruthenium catalyst systems are much more stable and have high functional group tolerance. There are many examples reported in the literature where ruthenium catalysed metathesis reactions are conducted in water or under air.<sup>13</sup> In 2005, the Nobel Prize in chemistry was awarded to Yves Chauvin, Richard R. Schrock and Robert H. Grubbs for their work with metathesis reactions. While, Chauvin was the first to propose the mechanism for olefin metathesis reaction.<sup>17a,b</sup> Schrock and Grubbs developed the first highly efficient

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molybdenum<sup>14</sup> and ruthenium<sup>15</sup> based metathesis catalysts, respectively. Nowadays, many metathesis catalysts have become commercially available and are widely used in industrial applications (Scheme 1).<sup>16</sup>



**Figure 1.** Some representative commercially available ruthenium based metathesis catalysts

The mechanistic studies of metathesis reactions have played an important role in catalyst development strategies.<sup>17</sup> For example, detailed mechanistic investigations of ruthenium catalyst systems assisted in the development of new ligands leading to higher functional group tolerance and improved activity. In the last twenty years, many different generations of Grubbs catalysts have been developed (1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> generation systems, Figure 1). Chauvin's general reaction mechanism of olefin metathesis represented an exciting way forward.<sup>17a,b</sup> He proposed that the reaction takes place via transition metal carbene complexes and metallacycles, whereby; the intermediates and the products are in equilibrium in the reaction mixture. As a result, the same metathesis catalyst and reactions can be used on industrial scale for the synthesis of 2-butene from propene (Philips Triolefin Process)<sup>18</sup> or, conversely, with the modification of experimental conditions, for the synthesis of high purity propene from 2-butene and ethylene (Olefin Conversion Technology).<sup>19</sup> Although various details of the mechanism of olefin metathesis reactions have already been disclosed, many questions still remain unanswered. Several examples of industrial-scale syntheses of value-added olefins having been reported to demonstrate wide applicability of the metathesis systems; however, there are still some limitations. For example the metathesis reaction of conjugated olefins is generally less efficient, often requires high catalyst loading and vigorous reaction conditions.<sup>20</sup> The development of economic and environmental benign catalytic processes enabling metathesis reactions with conjugated low value bio- or petrochemical-based raw materials to afford carbon dioxide neutral value added chemicals are of great industrial interest.<sup>21</sup>

Biographical Sketch.

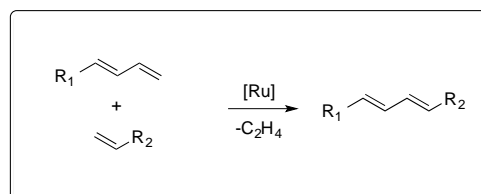
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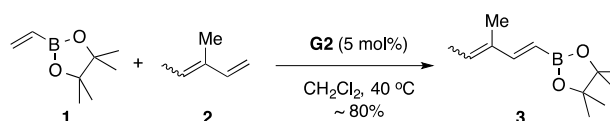
## 2. Representative examples for the conversion and synthesis of conjugated polyenes via olefin metathesis

**(1) Cross Metathesis (CM)-** Cross-metathesis is one of the most widely used chemical reactions for converting bio-based feedstock into value added chemicals (Scheme 1).<sup>22</sup> Nature is abundant in conjugated bond-containing bio-based materials such as conjugated polyunsaturated fatty acids, terpenes and chromophores.<sup>23</sup>



**Scheme 1.** General scheme for CM of conjugated olefins

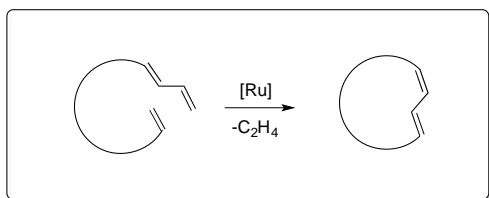
The chemoselective CM reaction of conjugated dienes has been investigated by Grubbs and co-workers.<sup>24</sup> They reported the reaction of vinyl boronate **1** with 3-methyl-1,3-pentadiene **2** affording the CM products with good yield (~80 %) and high chemoselectivity (88 – 100%) (Scheme 2). Moreover, they demonstrated that a wide range of functionalized conjugated dienes could be efficiently synthesized with high chemoselectivity at moderate reaction conditions.



**Scheme 2.** A representative example for the chemoselective conjugated olefin CM

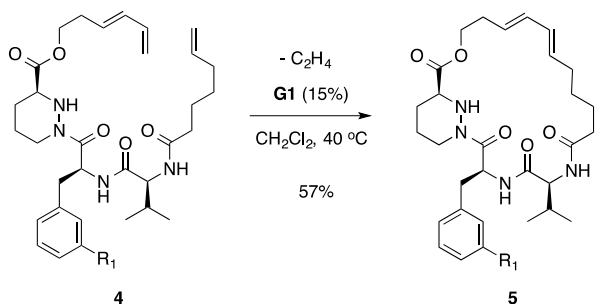
A recent review by Wojtkielewicz highlights the synthesis of conjugated polyenes using CM reactions.<sup>25</sup> The report summarises the synthesis of a wide range of natural product using conjugated olefin CM. However, the reactions required relatively high catalyst loadings (5–15%) and they had several limitations such as low regio- and stereoselectivity. The aforementioned limitations could be mitigated if one of the double bonds in the conjugated diene becomes electronically influenced or sterically hindered. If this takes place, then the affected double bond becomes less reactive allowing the metathesis reaction to proceed on the desired double bond providing high regioselectivity.<sup>24</sup>

**(2) Ring Closing Metathesis (RCM)-** Conjugated dienes are found in natural products and are very useful chemical intermediates. RCM of conjugated dienes can be chemo-selective as long as one of the double bonds is sterically hindered and thus, less favourable for the metathesis reactions. Nevertheless, the RCM reactions are simple and require mild reaction conditions (Scheme 3).



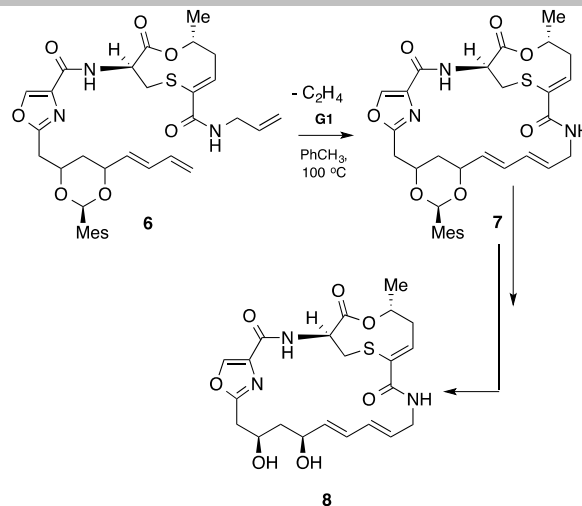
**Scheme 3.** General scheme for the RCM of conjugated olefins

The first example using RCM for the construction of macrocyclic 1,3-dienes was reported by Wagner and co-workers, in which the immunosuppressant Sanglifehrin **5** was synthesized from **4** using the **G1** catalyst at relatively high catalyst loading (15%) (Scheme 4).<sup>26</sup>



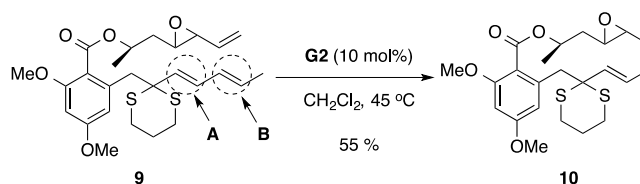
**Scheme 4.** Synthesis of Sanglifehrin **5** using conjugated diene RCM

Later, several groups reported the synthesis of conjugated diene unit-containing natural products and pharmaceuticals by RCM using **G1** and **G2** catalysts.<sup>26-29</sup> For example, the macrocyclic conjugated double bond containing griseoviridin **8** - type of Streptogramin antibiotic - was synthesized using RCM. Intermediate **7** was synthesized from starting material **6** by RCM using **G1** catalyst (Scheme 5).<sup>27</sup>



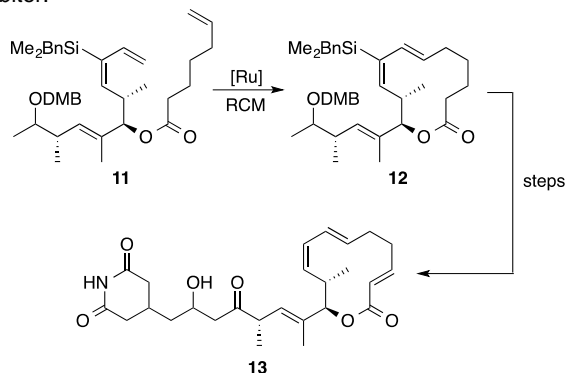
**Scheme 5.** Synthesis of griseoviridin **8** intermediate using conjugated diene RCM

Radicol is a natural product, which binds to HSP90 (Heat Shock Protein 90). HSP90 plays a key role in the regulation of cell growth in apoptosis and oncogenesis. Catalyst **G2** was used for the synthesis of radicol intermediate **10** from starting material **9** using RCM. Due to the sterically hindered, less reactive internal double bond **A** in **9** the metathesis reaction took place exclusively on olefinic bond **B** rendering high regioselective of the RCM reaction (Scheme 6).<sup>28</sup>



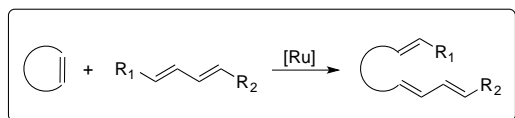
**Scheme 6.** Synthesis of radicol intermediate **10** using conjugated diene RCM

Another example of conjugated RCM is the synthesis of Lactimidomycin **13**. Intermediate **12** was synthesized from **11** using modified **HG2** catalyst system. High regio- and stereoselectivity of the macrocyclization reaction was achieved by strategic positioning of a silyl group on the diene unit. Lactimidomycin **13** shows antiproliferative properties against various tumours including human breast adenocarcinoma (Scheme 7), it acts as a potent cell-migration and translation inhibitor.<sup>29</sup>



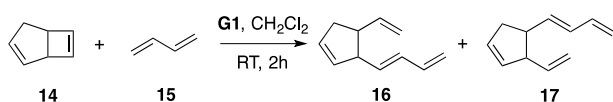
**Scheme 7.** Lactimidomycin **13** synthesized by ruthenium catalysed RCM

**(3) Ring Opening Cross Metathesis (ROCM)-** The only example, which can be found in the literature for the applications of ROCM using conjugated dienes (Scheme 8) is the synthesis of brown algae pheromones, viridienes species.



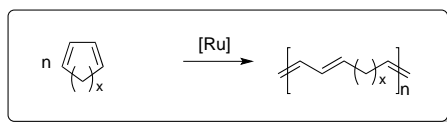
**Scheme 8.** ROCM reaction using conjugated diene substrates.

The reaction of bicyclo[3.2.0]hepta-2,6-diene **14** in presence of **G1** catalyst under an atmosphere of 1,3-butadiene **15** afforded a mixture of viridien **16** and isoviridien **17** (3:1, 42% overall yield) (Scheme 9).<sup>30</sup>



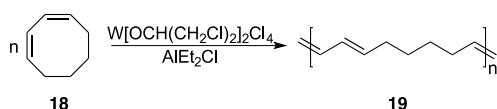
**Scheme 9.** Synthesis of viridien via ROCM

**4) Ring Opening Metathesis Polymerization (ROMP)-** Conjugated double bonds containing cyclopolyenes ROMP represents a remarkable method for the synthesis of conductive polymers for optoelectronics (Scheme 10).<sup>31</sup>



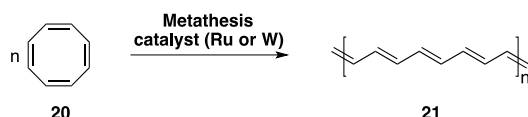
**Scheme 10.** A general demonstration of cyclic conjugated diene ROMP.

The ROMP of 1,3-cyclooctadiene **18** using  $W[OCH(CH_2Cl)_2]_2Cl_4$  -  $AlEt_2Cl$  catalyst has afforded a rubber like polymers **19** that contain conjugated double bonds (Scheme 11).<sup>32</sup>



**Scheme 11.** ROMP of 1,3-cyclooctadiene

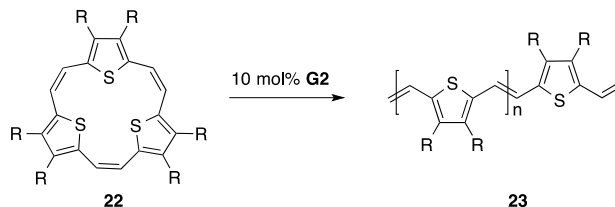
Ring opening metathesis polymerization of 1,3,5,7-cyclooctatetraene **20** (COT) was first reported with a well-defined tungsten metathesis catalysts. The reaction was carried out at ambient reaction condition in neat, affording polyacetylenes **21** in reasonable yield (Scheme 12).<sup>33</sup>



**Scheme 12.** ROMP of 1,3,5,7-cyclooctatetraene, formation of polyacetylene

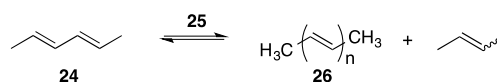
Attempts to polymerize **20** using **G1** catalyst did not result in any polymerization. However, using the **G2** ruthenium complex afford polymer **21** in 15-30% yield.<sup>34</sup> Turner and co-workers reported the ROMP of 2,3,8,9,14,15-

hexaoctyl[18]annulene-1,4,7,10,13,16-trisulfide **22** using **G2** catalyst (10 mol%) affording poly(3,4-dioctylthienylenevinylene) **23**.<sup>35</sup> The resulting polymers had high molecular weights, which were used to fabricate organic photovoltaic (OPV) devices showing power conversion efficiency of up to 0.18% (Scheme 13).



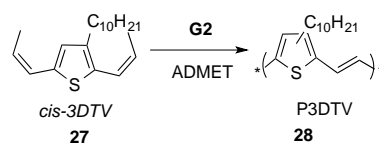
**Scheme 13.** ROMP of 2,3,8,9,14,15-hexaoctyl[18]annulene-1,4,7,10,13,16-trisulfide using the **G2** catalyst

**(5) Acyclic Diene Metathesis Polymerization (ADMET)-** ADMET polymerization is a step condensation reaction having wide range of application in polymer synthesis, in particular the synthesis of conjugated C=C double bond containing polymers.<sup>36</sup> Wagener and co-worker described the reactivity of conjugated monomers 2,4,6-octatriene and 2,4-hexadiene **24** in ADMET polymerization using Schrock's molybdenum catalyst- $Mo[CHC(C_6H_5)(CH_3)_2](N-2,6-C_6H_3-i-Pr_2)[OCCH_3(CF_3)_2]_2$  **25**. Polyenes **26** with similar physical properties and length were synthesized under identical reaction condition (Scheme 14).<sup>37</sup>



**Scheme 14.** Synthesis of methyl terminated polyene via ADMET polymerization of **24**

In addition, Hillmyer and co-workers reported on the use of ADMET polymerisation for the synthesis of high molecular-weight poly(2,5-thienylene vinylene) conducting polymers **28** from *cis*-2,5-Dipropenylthiophene **27** using **G2** catalyst (Scheme 15).<sup>38</sup>



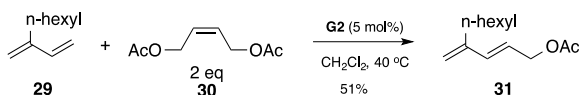
**Scheme 15.** ADMET of *cis*-2,5-Dipropenylthiophene **27**

These polymers have generated a great deal of interest due to their thermal and environmental stability, low bandgaps and high conductivity upon doping.<sup>39</sup>

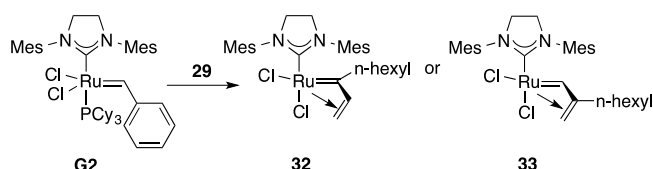
### 3. Scope

So far the available catalytic systems have limitations in the application of conjugated olefins<sup>1b,36</sup> especially polyenes in metathesis reactions due to issues regarding chemoselectivity.<sup>24</sup> One example is the reaction between a conjugated dienes and metathesis catalysts, which results in the formation of vinyl

alkylidene complexes. Upon intramolecular coordination of the allyl ligands a  $\eta^3$ -allyl, a less active metathesis catalyst may form. For example, significant amount of unreacted 2-hexyl 1,3-butadiene **29** remained in the CM reaction with (Z)-but-2-ene-1,4-diyl diacetate **30** at 40 °C reaction temperature indicating that the catalyst may have shut down before the reaction completed (Scheme 16 and 17). However, when the reaction was carried out at elevated temperatures, a significantly higher conversion was observed. It was proposed that the elevated temperature may have weakened the alkene-ruthenium coordinative bond **32**, **33** which in turn allowed the less reactive ruthenium intermediate to re-enter the catalytic cycle.<sup>40</sup>



**Scheme 16.** CM of **29** and **30** with catalyst **G2**



**Scheme 17.** Tentative formation of less active vinyl alkylidene ruthenium complexes **32** and **33**

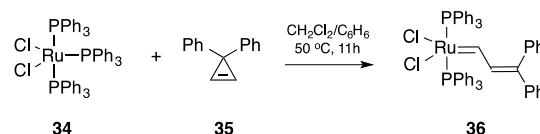
The scope of this manuscript is to summarize the fundamental research, mechanistic approach and preliminary work that have been completed in the field of conjugated polyene metathesis. This may open a new way for the utilization of conjugated petrochemical by-products as well as carbon dioxide neutral (renewable) resources. Moreover, the molecular understanding of the reversible formation of  $\eta^3$  -  $\eta^1$ -allyl complexes could provide opportunities for the development of a new generation ruthenium based latent metathesis catalyst systems.

Catalysts that show activity only under external stimuli (heat, light, or sound) are called "latent catalysts". In particular, photochemically and thermally initiated catalytic processes are considered to be among the most important for practical use. An important characteristic of a latent polymerization catalyst is that the initiation and propagation step can be controlled by external stimulation. It is envisioned that this feature of a potential latent polymerization catalyst may lead to "programmable" polymer, co-polymer and block-polymer architecture design and well-defined macromolecular structure fabrication.<sup>41</sup>

#### 4. Synthesis and investigation of $\eta^1$ - and $\eta^3$ -allyl ruthenium metathesis active complexes

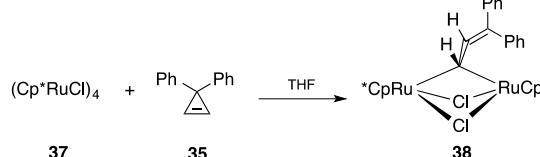
Molecular level mechanistic understanding of conjugated olefin metathesis is crucial for the development of next generation, highly active allyl ruthenium catalyst systems. In this section the synthesis of allyl ruthenium complexes as potential intermediates or pre-catalysts for conjugated olefin metathesis reactions are summarized. One of the earliest, well-defined ruthenium based metathesis catalyst,  $(\text{PPh}_3)_2(\text{Cl})_2\text{Ru}(\text{=CHCH=CPh}_2)$  **36** comprises of a  $\eta^1$ -allyl unit.

Its activity was far lower than current metathesis catalysts. However, it did show catalytic activity in ROMP of norbornene. The complex was synthesized by the reaction of 3,3-diphenyl cyclopropene **35** with either  $\text{RuCl}_2(\text{PPh}_3)_4$  **43** or  $\text{RuCl}_2(\text{PPh}_3)_3$  **34** (Scheme 18).<sup>42</sup>



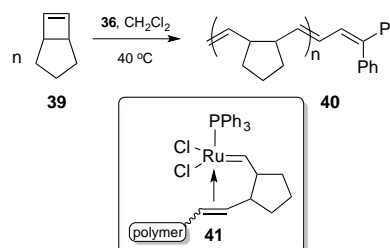
**Scheme 18.** Synthesis of the first well-defined  $\eta^1$ -allyl ruthenium metathesis catalyst **36**

Following a similar approach, the reaction of excess 3,3-diphenyl cyclopropene with  $(\eta^5\text{-C}_5\text{Me}_5\text{RuCl})_4$  **37** gave a bridging vinyl carbene ruthenium complex  $([\eta^5\text{-C}_5\text{Me}_5\text{RuCl}]_2\text{=CHCH=CPh}_2)$  **38**. Although the formed complex reacted very well with strained olefins, due to the bridging nature of the alkylidene, the ruthenium complex was shown to greatly diminish the activity of the olefin metathesis (Scheme 19).<sup>43</sup>



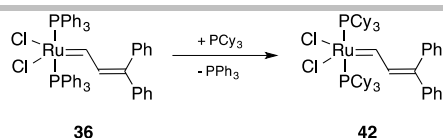
**Scheme 19.** Synthesis of  $([\eta^5\text{-C}_5\text{Me}_5\text{RuCl}]_2\text{=CHCH=CPh}_2)$  complex **38**

Grubbs and co-workers reported the polymerization of bicyclo[3.2.0]hept-6-ene **39** using the catalyst **36**, this afforded the atactic polymer **40** in a controlled manner. It was reported that during the polymerization the dissociation of the phosphine was aided by the chelation of the double bond on the growing polymer chain resulting in a five-membered ring (complex **41**, Scheme 20).<sup>44</sup>



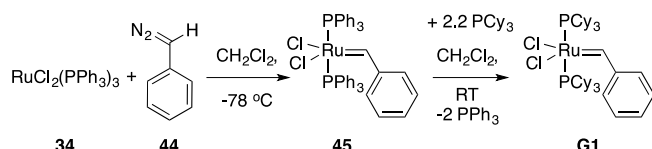
**Scheme 20.** Polymerization of bicyclo[3.2.0]hept-6-ene and the tentatively supposed chelated intermediate **41**

Although the activity of **36** was demonstrated in several ROMP reactions, it was still not suitable for the metathesis of acyclic olefins. However, it was found that tuning of the electronic factors on the catalyst active centres influenced the metathesis activity of the ruthenium complexes. It was demonstrated that using electron-rich ancillary ligands increases the metathesis activity. Replacement of the triphenyl phosphine ligand by alkylphosphines, such as tricyclohexyl phosphine ( $\text{PCy}_3$ ), a better  $\sigma$ -donating ligand, provided a ruthenium complex **42** with high metathesis activity (Scheme 21).<sup>45</sup>



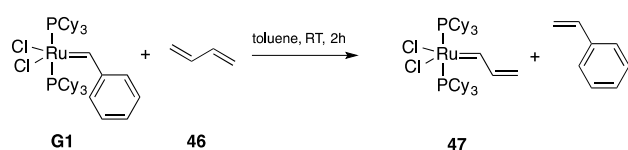
**Scheme 21.** Synthesis of first well-defined  $\eta^1$ -allyl ruthenium catalyst **42** for metathesis of acyclic olefins.

The catalytic activity of **42** was demonstrated not only on a wide range of olefin metathesis,<sup>46</sup> but also on several enyne cross metathesis reactions.<sup>47</sup> In the past years intensive research work was carried out in the field of olefin metathesis to develop new catalysts. Although complex **42** demonstrated remarkable stability towards many different functional groups, oxygen and protic solvents, the synthetic procedure of **36**, - the precursor of **42** - had many limitations in the wide spread application of this form of olefin metathesis. While the metathesis catalyst **42** can be synthesized in reasonable to good yields (Scheme 18 and 21), the relatively inaccessible reagent **35** rendered only low scale applications. An alternative synthetic procedure to the one shown in scheme 18, is the reaction between **34** and (diazomethyl)benzene **44**. Complex **45** undergoes a ligand exchange of PCy<sub>3</sub> affording **G1** catalyst (Scheme 22).<sup>48</sup>



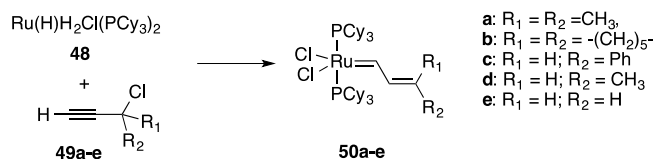
**Scheme 22.** Synthesis of **G1** catalyst using (diazomethyl)benzene

The (PCy<sub>3</sub>)<sub>2</sub>(Cl)<sub>2</sub>Ru(=CHCH=CH<sub>2</sub>) **47** complex was synthesized by reacting the **G1** catalyst with butadiene (**46**) (Scheme 23). It was found that the reaction leads to the formation of a stable  $\eta^1$ -allyl type complex. The complex **47** was less reactive toward acyclic olefins than **42**. However, it did show some catalytic activity for the ROMP of cyclooctene and norbornene.<sup>49</sup>



**Scheme 23.** Reaction of **G1** catalyst with butadiene

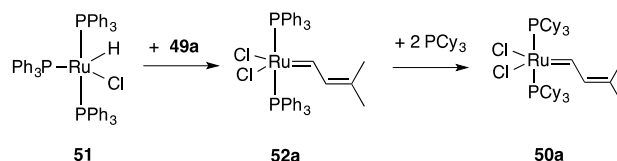
It has been demonstrated that ruthenium hydride complexes<sup>50</sup> can be used to generate metathesis active ruthenium carbene species. It was found that Ru(H)H<sub>2</sub>Cl(PCy<sub>3</sub>)<sub>2</sub> **48** reacts with 3-chloro-3,3'-dialkyl-1-butyne **49a-e** to afford (PCy<sub>3</sub>)<sub>2</sub>(Cl)<sub>2</sub>Ru(=CHCH=CR<sub>1</sub>R<sub>2</sub>) **50a-e** (Scheme 24).<sup>52</sup>



**Scheme 24.** Synthesis of the well-defined  $\eta^1$ -allyl ruthenium metathesis catalysts via a ruthenium hydride complex **48**

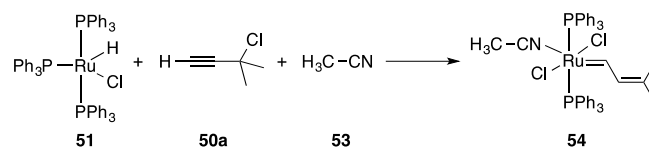
So far the mechanism of carbene formation has not been investigated in a great detail; however, literature reviews have speculated that the first step of the reaction involves the insertion of the alkyne between the Ru-H bond.<sup>53</sup> Fogg and his co-workers in 2002 reported the formation of Ru(H)<sub>2</sub>(Cl)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> as a side product. It was found that the amount of this complex increases as less bulky R<sub>1</sub> and R<sub>2</sub> ligands are introduced. The ratio of the carbene species was significantly increased when the solvent was changed from dichloromethane to toluene.

Alternatively, **50a-e** can be synthesized by the reaction of commercially available Wilkinson type Ru(H)Cl(PPh<sub>3</sub>)<sub>3</sub> **51** complex with 3-chloro-3-methyl-1-butyne **49a** followed by phosphine (PCy<sub>3</sub>) exchange (Scheme 25).<sup>54</sup>



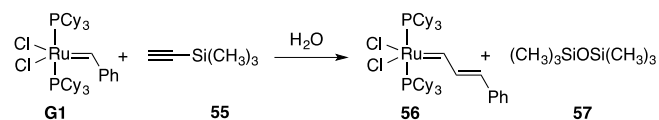
**Scheme 25.** Synthesis of (PCy<sub>3</sub>)<sub>2</sub>(Cl)<sub>2</sub>Ru(=CHCH=C(CH<sub>3</sub>)<sub>2</sub>) **50a** via RuHCl(PPh<sub>3</sub>)<sub>3</sub>

It has also been demonstrated by Hofman and co-workers that in the presence of acetonitrile **53** a hexa-coordinate acetonitrile ruthenium complex **54** can form (Scheme 26).<sup>55,56</sup>



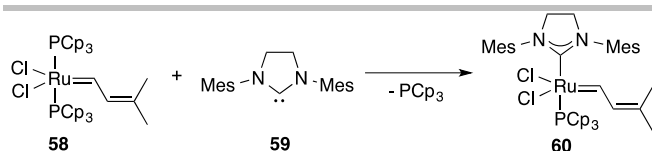
**Scheme 26.** Synthesis of (PPh<sub>3</sub>)<sub>2</sub>(Cl)<sub>2</sub>Ru(=CHCH=C(CH<sub>3</sub>)<sub>2</sub>)(CH<sub>3</sub>CN) **54** complex

Powala et al. recently reported the reaction of **G1** with silylacetylenes (HCCSi(CH<sub>3</sub>)<sub>3</sub>) **55** resulted in a vinyl carbene complex (PCy<sub>3</sub>)<sub>2</sub>(Cl)<sub>2</sub>Ru(=CHCH=CHPh) **56**, and disiloxane **57** with high yields (up to 84%).<sup>57</sup> The reaction was carried out using 4Cl, 4Br and 4OMe functionalized benzylidene ligands containing complexes. The reaction took place via carbon-silicon bond cleavage in the presence of water. This method represents a simple alternative way to synthesize  $\eta^1$ -allyl ligand containing Grubbs catalyst systems (Scheme 27).<sup>58</sup>



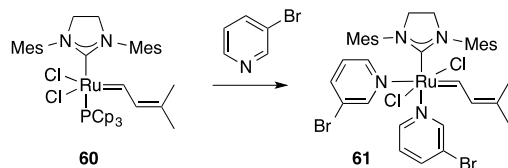
**Scheme 27.** Synthesis of (PCy<sub>3</sub>)<sub>2</sub>(Cl)<sub>2</sub>Ru(=CHCH=CHPh) **56** complex

Scholl et al. and others have shown that when replacing PCy<sub>3</sub> or PCp<sub>3</sub> ligands with 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (NHC) **59** (Scheme 28) an increased metathesis catalytic activity is achieved.<sup>59</sup> Similar reactions can be carried out with **52a** leading to the formation of PPh<sub>3</sub> phosphine-NHC ligand containing metathesis catalysts.<sup>60</sup>



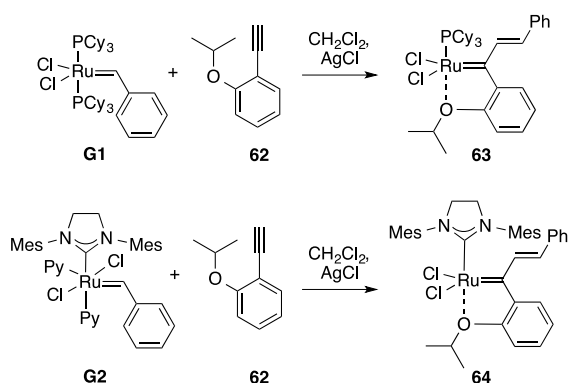
**Scheme 28.** Synthesis of  $\eta^1$ -allyl ruthenium NHC complex **60**

A new dimethylvinyl carbene complex **60** was reported by Akvan and co-workers, the displacement of  $\text{PCp}_3$  with 3-bromopyridine afforded the complex **61** (Scheme 29). This catalyst is active in ADMET and ROMP polymerization. The formed complex **61** is actually the analogue of the highly metathesis active catalyst **G3**. The reaction kinetics of **61** with ethyl vinyl ether (EVE) has been investigated. The experimental results demonstrated a rapid, much faster initiation than **60**.<sup>61</sup>



**Scheme 29.** Synthesis of complex **61**.

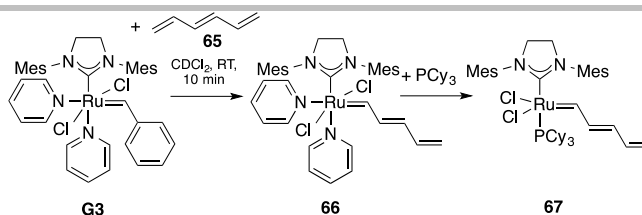
Hansen et al. reported the reaction of **G1** and **G2** catalyst with 1-ethynyl-2-isopropoxybenzene **62** resulting in the formation of bidentate vinyl carbene species **63** and **64**.<sup>62</sup> These complexes can be considered as  $\eta^1$ -allyl ligand containing Hoveyda-Grubbs catalyst systems. The complexes are catalytically competent materials due to the *ortho*-isopropoxy group, which presumably suppresses the formation of the catalytically inactive  $\eta^3$  species (Scheme 30).<sup>63</sup>



**Scheme 30.** Synthesis of  $\eta^1$ -allyl Hoveyda-Grubbs complexes

The olefin metathesis for metal incorporation (OMMI) – actually olefin-metal stoichiometric reaction – has not been successful when using **G2** complex. This can easily be understood based upon the mechanistic investigation data reported by Grubbs indicating that the activity of **G2** is limited by the slow initiation step, corresponding to the loss of  $\text{PCy}_3$  from the complex.<sup>64</sup>

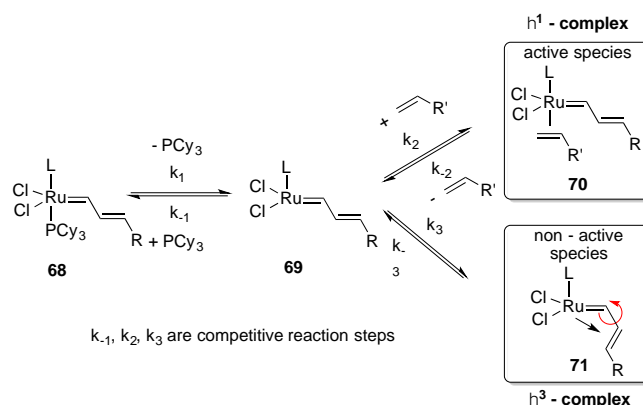
However, as the initiation of **G3** complex is significantly faster than those of **G2**, the stoichiometric reaction of **G3** with conjugated polyolefins can easily lead to OMMI complexes. It has been reported by Sponsler and co-workers that the reaction of **G3** with hexatriene **65** followed by the addition of  $\text{PCy}_3$  results in the formation of  $\eta^1$ -allyl **G2** derivative complex **67** (Scheme 31).<sup>65</sup>



**Scheme 31.** Synthesis of  $\eta^1$ -allyl analogues of 2<sup>nd</sup> and 3<sup>rd</sup> generation Grubbs complexes **66** and **67**

## 5. Mechanistic considerations

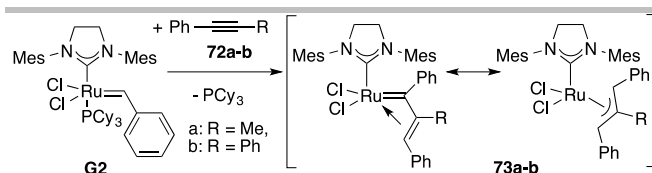
In order to optimize the catalyst systems we need to understand the fundamental steps of the catalytic cycle. As it was described in the introduction, the reported metathesis reactions of conjugated polyenes are limited. One of the hypotheses is that if a conjugated diene reacts with a catalyst to form vinyl alkylidene **68**, then due to intramolecular coordination a less active, stabilized  $\eta^1$ -allyl ruthenium catalyst **71** may form (Scheme 32). Even if the  $\eta^1$  -  $\eta^3$ -allyl coordination is reversible then there is a competitive step between the olefin substrate **70** and intramolecular allyl bond **71** coordination. This competition certainly reduces the catalyst's overall performance.



**Scheme 32.** Competitive reaction steps resulting in metathesis catalyst activity reduction

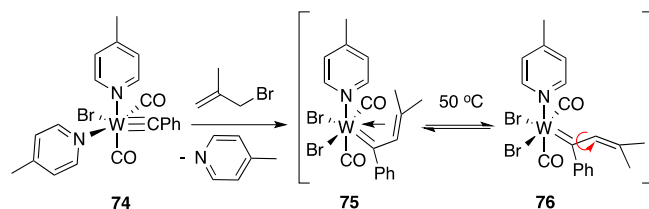
Ruthenium  $\eta^1$ -allyl complexes **73a-b** have already been reported by Grubbs and co-workers, which have formed in the reaction between **G2** and acetylenes **72a-b** (Scheme 33).<sup>66</sup> The  $\eta^1$  -  $\eta^3$ -allyl conversion was investigated and it has been reported that  $\eta^1$ -allyl species formation could not be detected even at 130 °C. The X-ray structure analysis of the isolated  $\eta^1$ -allyl ruthenium complex revealed that the arrangement of the chlorines around the Ru atom is unusual. One of the chlorines is almost perpendicular to the  $\text{Cl-Ru=CR'R''}$  plane (Figure 2, B); however, according to recent X-Ray studies and other reported literature findings, the highly active (i.e.  $\text{Cl}_2\text{Ru=CHPh}$  or  $\text{Cl}_2\text{Ru=CH}_2$ ) catalyst species both chlorines and  $\text{Ru=C}$  bonds can be found in one plane (Figure 2, A).<sup>67</sup> This is an indication that the formation of stable allyl  $\eta^3$ -allyl bond has significant impact on the active molecule core structure.





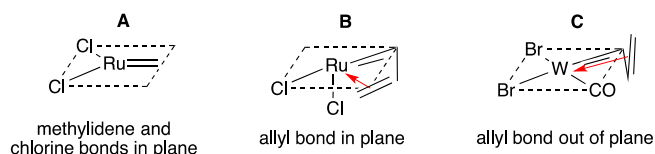
**Scheme 33.** Formation of  $\eta^3$ -allyl Ru NHC complex reported by Grubbs

The reactivity of **73a-b** with nucleophilic agents was investigated and reported by Trnka et al. It was found that complexes **73a-b** only react with ethylene and no other olefins. On the other hand, catalyst decomposition and diene formation was observed. The reaction with pyridine resulted in the formation of  $(\text{H}_2\text{IMes})(\text{py})_3(\text{Cl})_2\text{Ru}$ .<sup>68</sup> This is a clear indication that the  $\eta^3$ -allyl bond can be unfolded by strong nucleophiles. It is known that the  $\eta^1 - \eta^3$  conversion of transition metal allyl complexes is an equilibrium reaction, which can be shifted in the desired direction with the appropriate modification of the reaction conditions.<sup>69</sup> Presumably, in case of the ruthenium allyl complexes similar equilibrium exists. The allyl systems for tungsten complexes are also known and some complexes have been reported to have dynamic intermolecular rearrangement.<sup>70</sup> VT NMR investigations have shown that the reported  $\eta^3$ -allyl systems **75** can be converted to  $\eta^1$  **76** when the temperature is increased to 50 °C. The X-ray structure have revealed that  $\text{W}=\text{C}$  and allyl  $\text{C}=\text{C}$  bonds are oriented almost perpendicular to each other and thus, the classical  $\eta^3$ -allyl type electron delocalization is not involved. The authors explained this unusual  $\eta^3 - \eta^1$  conversion by proposing a very weak metal-allyl interaction (Scheme 34).



**Scheme 34.** Synthesis of  $\eta^3$ -allyl tungsten complex **75** and **76** and its proposed dynamic behaviour

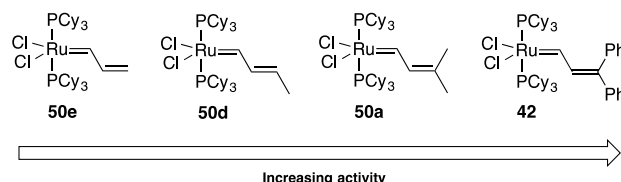
According to the detailed structure analysis of the  $\eta^3$ -allyl ruthenium complex **73a-b** (Figure 2, B), it can be concluded that the carbene double-bond and the vinyl bond are almost coplanar, which is ideal for the  $\eta^3$ -allyl delocalization. However, it is not the case for the tungsten complex **75** (Figure 2, C) whereby the vinyl bond is out of the plane.



**Figure 2.** General scheme for the arrangement of vinyl bonds in Ru and W coordination sphere

This might explain that even at high temperatures, there is no  $\eta^3 - \eta^1$  allyl bond dissociation observed for the ruthenium allyl complex **73a-b**, although it exists for the tungsten allyl complexes **75**, **76** at ambient temperature.

It is known that the reactivity of ruthenium alkyl vinylidenes (ruthenium allyl complexes) in metathesis is lower than that of  $(\text{PCy}_3)_2(\text{Cl})_2\text{Ru}(\text{=CHPh})$  or  $(\text{PCy}_3)_2(\text{Cl})_2\text{Ru}(\text{=CHCH}_3)$ .<sup>71</sup> If we consider the catalytic activities of the first generation **G1** derived metathesis catalysts it can also be easily recognized that increasing the bulkiness of the R groups improves catalytic activity of the allyl complexes. For example the diphenyl vinylidene **42** and dimethyl vinylidene **50a** complexes are highly active in ROMP and RCM reactions. However, the non-substituted vinylidene complex **50e** shows significantly less activity in metathesis reactions (Figure 3).



**Figure 3.** Stable  $\eta^1$ -allyl ruthenium complexes

This suggests that the vinyl bond coordination is weaker when bulky allyl systems are used and the catalyst olefin substrate coordination step competes with the vinyl group “back-biting” ( $\eta^3$ -allyl complex formation).

## 6. Summary and Outlook

Development of environmentally benign chemical processes and technologies are central issues to both academia and industry. The use of fossil fuels based raw materials increase greenhouse gas emissions in the atmosphere resulting in serious climate changes. The development of  $\text{CO}_2$  neutral fuels and materials is one of the most urgent challenges facing our society. Olefin metathesis is a powerful and versatile environmentally benign method in synthetic organic and polymer chemistry. Most of the reactions take place at ambient condition and the atom economy of these synthetic procedures is high (often 100%), indicating that most of the starting materials are incorporated into the end products. Nature is abundant in conjugated bond containing bio-based materials. Low value added conjugated olefins can also be found in vast amount in petrochemical by-products. These chemicals often render an underutilized feedstock. This review summarized the pioneering work in the field of conjugated olefins metathesis and the fundamental mechanistic investigations that illustrates the formation of ruthenium  $\eta^3$ - and  $\eta^1$ -vinylcarbene intermediates. The thorough investigation of the chemical behaviour of ruthenium vinylcarbene complexes will certainly open new alternatives in latent olefin metathesis catalyst development.

The journey on this highly fruitful and relevant scientific research field should provide alternative solutions in the development of carbon-dioxide neutral and green chemical processes.



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**Keywords:** olefin metathesis • ruthenium • conjugated olefins • allyl complex • latent catalysts

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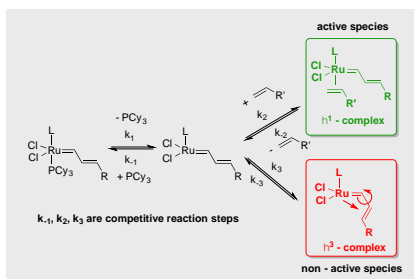
## Entry for the Table of Contents (Please choose one layout)

Layout 1:

### MINIREVIEW

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The understanding of the mechanism of ruthenium NHC  $\eta^1$  -  $\eta^3$ -allyl complexes' interconversion may open the way to the development of new generation ruthenium based latent metathesis catalyst systems. This review summarizes the most relevant pioneer work focused on conjugated polyene metathesis in order to open new ideas for the development of forthcoming metathesis catalyst and exploring different application areas.



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Antisar Hlil, Hassan S. Bazzi and Robert  
Tuba\*

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**Ruthenium Catalyzed Metathesis of  
Conjugated Polyenes**